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I, LEANNE MYNOTT, MANAGER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. 2003906985 for a patent by SMART TECHNOLOGIES PTY LTD as filed on 18 December 2003.



WITNESS my hand this
Eleventh day of January 2005

A handwritten signature in black ink, appearing to be 'L. Mynott'.

LEANNE MYNOTT
MANAGER EXAMINATION SUPPORT
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The invention is described in the following statement:

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Method for electrolytic engineering of nano-particulate layers

This invention relates to nano-structured materials and their applications; to methods for the production of such materials. More particularly, this invention relates to nanostructured layers formed on a substrate.

BACKGROUND TO THE INVENTION

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The nanomaterials, in particular- nanooxides are used in wide range of applications: sensors, batteries, capacitors, photovoltaic cell (e.g. Dye Solar Cells), electrochromic devices, fuel cells and devices for photocatalytic cleavage and purification of water.

High commercial potential of Dye Solar Cell technology is achieved through nano-particulate structure of oxide layer, that warrants high surface area, and, thus, - high ability to adsorb sufficient quantity of dye to effectively capture solar light on interface between the dye layer and electrolyte.

It has been recognized that surface properties of nano-particles are critical for achieving high performance of devices based on nano-particulate materials.

Modifications of the said properties can be performed by

covering each particle by a thin layer of another material. The purpose of such covering varies. This include:

5 Creating of a barrier layer (e.g. junction between two materials with different electronic properties). Benefits of the barrier layer include creation of internal electrical field, that allows for unidirectional transfer of electrons (diode effect).

10 Creating a blocking layer (electrically insulation of full or part of the surface of a particle from electrolyte).

Deposition of light absorbing materials

Etc.

15 Electronic shielding of nano-structured oxides. Certain materials that reside adjacent to the surface of the said NSO provide electronic shielding of the said surface, and thus prevent undesirable charge transfer through the interface between the said surface and an electrolyte.

The said charge transfer causes undesirable side reactions that lead to degradation of a device. Preferably the said
20 Electronic Shielding Materials (ESM) are optically transparent and chemically stable.

Current methods include sol-gel chemistry and vacuum deposition. Both techniques are limited as they do not
25 allow for fast and precise deposition and achieving desirable properties of the layers.

Objectives of the Invention

30 An objective of the present invention is to provide methods for surface modifications of nano-oxides.

SUMMARY OF THE INVENTION

From one aspect, the present invention involves formation of nano-particulate layers on an electrically
5 conductive substrate directly from a colloidal solution by application of negative electrical potential to the substrate and positive electrical potential to a counter electrode. The nano-particles are further interconnected by either sintering in furnace or by applying an AC
10 electrical field of sufficient magnitude, such as high local current passing between particles are heating local contact points and fusing the particles together.

From another aspect of the invention, the nano-oxide
15 layer is coated by dye. The coating is applied by immersing the electrode into the dye solution and applying electrical field that promotes movement of dye in the solution towards the nano-oxide layer and subsequent attaching dye to the said nano-oxide particle.

20 In one embodiment in accordance with this aspect of the invention, the application of dye is followed by application of another dye or of another absorber that blocks areas of the nano-oxide that had not been covered
25 by the first application of dye. The application of another dye or that of another absorber is conducted in the same manner as that of the first dye, e.g. - from solution and with aid of electrical field of appropriate polarity.

30 From further aspect of the invention, a barrier layer is formed on surface of the said nano-oxide. The barrier layer typically comprises metal oxide, electronic properties of which differ from that of original nano-

oxide of the nano-particulate layer. Application of such barrier layer is conducted in solution by creation of electrical field that promotes movement of material of the barrier layer towards nano-particles with subsequent
5 deposition of this material on surface of the said nano-particles.

In one embodiment in accordance with this aspect of the invention more than two layers with different
10 electronic properties are deposited to create several barrier layers of desired properties.

In further embodiment in accordance with this aspect of the invention, the substrate is treated by heat and/or by oxygen to ensure good attaching of the deposited layers
15 to the nano-particles and/or oxidation of the deposited material.

From another aspect of the invention an electrolytic treatment is used to modify surface properties of nano-
20 oxide. In one embodiment a clean an active surface of the nano-particles is achieved by electrolytic dissolution of surface material. In another embodiment an electrolytic oxidation ensures carbon free layers of the nano-particulate material.

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From yet another aspect of the invention the electrolytic deposition as disclosed above is conducted under constant current conditions with imposed voltage limits, such as when voltage reaches predefined limit
30 (measured with respect to the reference electrode) a control circuitry switches from the constant current to the constant voltage mode, keeping the constant voltage mode until either current drops below predetermined value

or predetermined amount of electrical charge passes through the electrolytic solution.

It has been found advantageous to perform the said deposition in series of cycles with progressive increase of charge transferred through the electrolyte solution. Each cycle comprises an insertion and extraction half-cycle. During the insertion half-cycle a material to be deposited is promoted by electrical field towards the nano-particulate oxide. During the extraction half-cycle the material is removed from the nano-particulate oxide. Both insertion and extraction half-cycle are performed under current limiting conditions until the voltage reaches a voltage preset magnitude, continuing deposition under voltage limiting conditions until either the deposition current falls to a current preset magnitude or a preset charge has been delivered, and then terminating deposition.

It has been found advantageous to superimposes the constant current/constant voltage insertion/extraction mode with an applied AC electrical field. In one example the AC electrical field is applied parallel to the substrate, in another example - perpendicular to the substrate.

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